STATE OF OHIO
George V. Voinovich, Governor
DEPARTMENT OF NATURAL RESOURCES
Donald C. Anderson, Director
DIVISION OF GEOLOGICAL SURVEY
Thomas M. Berg, Chief

Information Circular No. 59

LIMESTONE AND DOLOMITE AVAILABILITY IN THE OHIO RIVER VALLEY FOR SULFUR SORBENT USE, WITH OBSERVATIONS ON OBTAINING RELIABLE CHEMICAL ANALYSES

by
David A. Stith, Thomas M. Berg, Curtis H. Ault,
Garland R. Dever, Jr., John M. Masters, Samuel W. Berkheiser, Jr.,
Claudette M. Simard, and Norman C. Hester

OHIO VALLEY MINERAL CONSORTIUM

ILLINOIS STATE GEOLOGICAL SURVEY
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Columbus
1997

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ABSTRACT

Large quantities of carbonate rock are available as sulfur sorbents in the six states along the Ohio River Valley. Many choices with respect to controlling SO_2 and mitigating acid in air and water need to be made for the future and our environment. Detailed geologic maps and carbonate-availability assessments are needed to provide data for these choices.

High-purity dolomite and high-calcium limestone are common in some parts of the region and scarce in others. The available resources of limestone greatly increase as the specified level of $CaCO_3$ drops below 95 percent. Much published and unpublished information is available at the six state geological surveys of the Ohio Valley, including chemical analyses on more than 18,000 limestone and dolomite samples.

The American Society for Testing and Materials issues several standards relevant to chemical analysis of carbonate rocks. Several methods of chemical analysis provide reliable compositions of carbonate rocks when the analyses are done properly. The key to obtaining a reliable analysis is the use of proper quality-assurance and quality-control techniques, both in the analytical method and in the laboratory-selection and sample-submission procedures.

INTRODUCTION

The six states bordering the Ohio River—Illinois, Indiana, Kentucky, Ohio, Pennsylvania, and West Virginia—are the traditional industrial heart of the United States, partly because of the availability of abundant coal resources for electrical power generation. Coal-fired power plants generate more than half of the electricity produced in the U.S., and the plants in the Ohio Valley states account for about a third of that production.

The impacts of the Federal Clean Air Act Amendments of 1990 are clearly felt. The locally abundant deposits of limestone and dolomite in the Ohio Valley may be an important resource to control SO_2 emissions from the numerous coal-fired power plants of the region. In 1991, the six states of the Ohio Valley had 50 coal-fired generating units in operation using scrubbers. These plants had more than 23,000 megawatts (MW) of generating capacity. Also, four of the states had over 900 MW of capacity from fluidized-bed combustors (figs. 1 and 2).

The state geological surveys of Illinois, Indiana, Kentucky, Ohio, Pennsylvania, and West Virginia, assisted by the aggregate and crushed-stone associations of the region, formed the Ohio Valley Mineral Consortium in 1992 to promote the need for cooperation and research in SO_2 emission control. This report was compiled by the Consortium and is adapted from a paper presented at the National Stone Association SO_2 Capture Seminar, "Sorbent Options and Considerations," held in Cincinnati, Ohio, September 19-21, 1993.

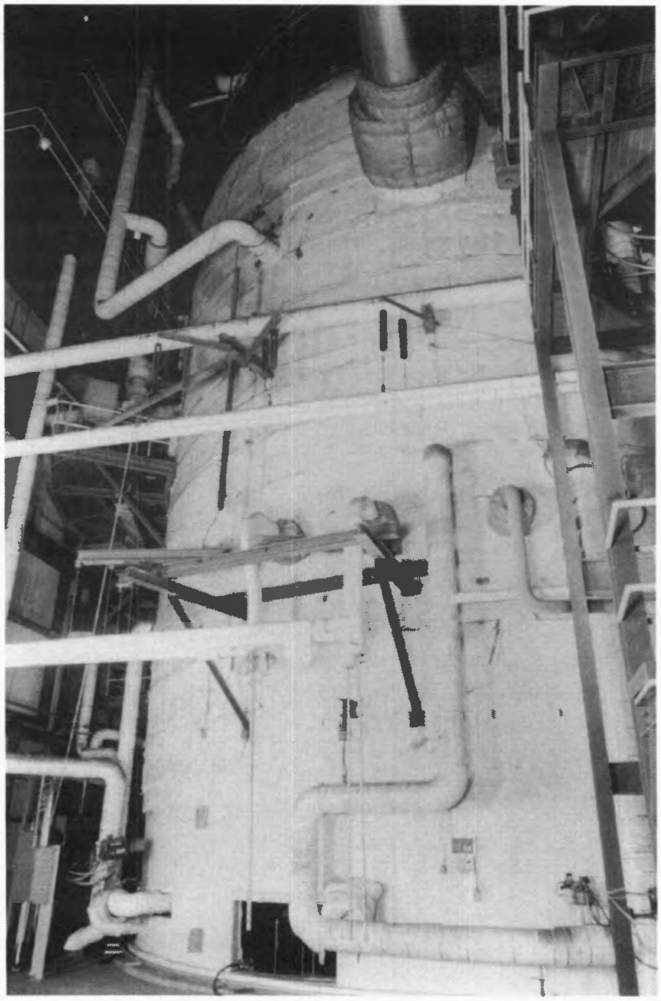

FIGURE 1.—Combustor vessel of the pressurized fluidized-bed combustion (PFBC) boiler of the Tidd Demonstration Plant, American Electric Power Service Corporation (AEP), near Brilliant, Jefferson County, Ohio. This demonstration plant has a 70-MW generating capacity. The pressure vessel encloses the boiler and cyclones and is 70 feet high and 44 feet in diameter. Photograph courtesy of AEP.

ACKNOWLEDGMENTS

Kim E. Vorbau, Ohio Division of Geological Survey, digitized the maps for figures 3, 5, 8, 11, and 12. Lisa R. Smith, Illinois State Geological Survey, prepared the computerized

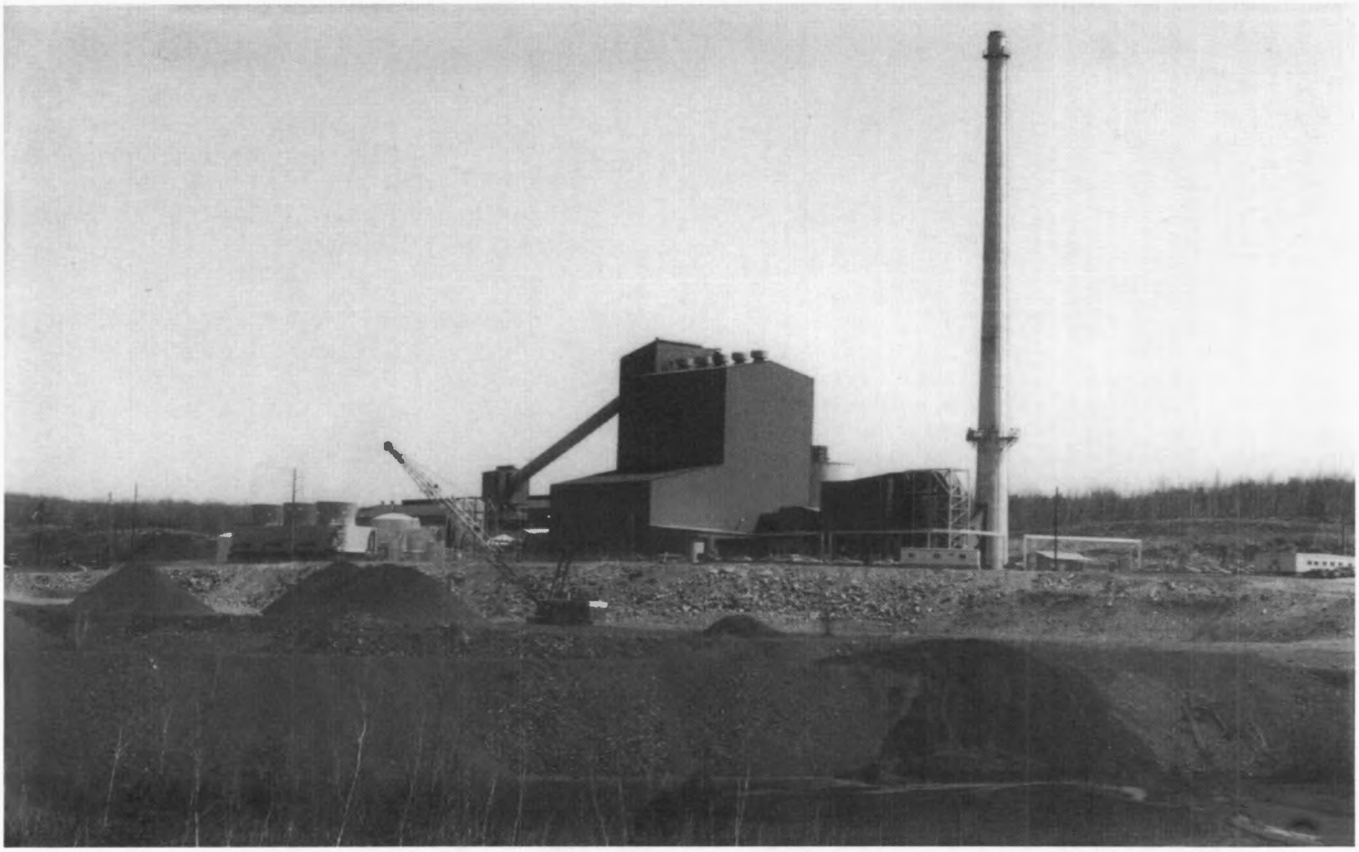

FIGURE 2.—Cogeneration plant using a circulating fluidized-bed combustion (CFBC) boiler in Schuylkill County, Pennsylvania. The 42-MW plant of the Wheelabrator Frackville Energy Company uses 25,000 to 30,000 tons of carbonate rock per year in burning 500,000 tons of anthracite waste. Photograph courtesy of Jon Inners (Pennsylvania Geological Survey).

base maps for the Illinois quality maps. Appreciation also is expressed to the many persons from state geological surveys, limestone producers, and commercial laboratories who were contacted for their views on the reliability of carbonate-rock chemical analysis.

LOCATION OF RESOURCES

Carbonate rocks (limestone and dolomite) of varied purities are abundant in the six states bordering the Ohio River. Although these supplies are large, their location is dictated by geological conditions and not by their proximity to potential users for acid mitigation and SO_2 control.

The general outcrop belts of carbonate rock in the Ohio Valley states are shown in figure 3. The outcrop patterns in the region are quite varied. Carbonate resources in Pennsylvania mainly consist of narrow, folded bands of steeply dipping Cambrian to Devonian limestone and dolomite in the southeastern, central, and south-central parts of the state. In addition, there is a flat-lying Pennsylvanian limestone in the western part of the state that is sufficiently thick to quarry.

In West Virginia, steeply dipping carbonate rocks primarily occur as narrow, folded bands in the Great Valley, Valley and Ridge, and Appalachian Plateaus Physiographic Provinces in the eastern and southeastern parts of the state. Minor thin, flat-lying Pennsylvanian limestones occur in the western two-thirds of the state. Approximately half of the carbonate rock produced in West Virginia is Mississippian limestone; there are lesser amounts of Cambrian to Devonian limestone and dolomite.

The western half of Ohio contains extensive, flat-lying deposits of Silurian dolomite and lesser amounts of Devonian limestone and dolomitic limestone and Silurian limestone. Minor amounts of thin, relatively flat-lying Pennsylvanian limestone are found in eastern Ohio.

Flat-lying Mississippian limestones crop out through much of south-central Indiana. In addition, a broad band of Silurian and Devonian dolomite stretches across much of northern, eastern, and southeastern Indiana. Isolated patches of limestone also occur in this region.

Kentucky has extensive deposits of Mississippian limestone in the western, south-central, east-central, and southeastern parts of the state. Ordovician limestone and dolomite and Silurian dolomite are mined and quarried in central Kentucky. Mississippian limestone from western Kentucky, principally the Ste. Genevieve Limestone, is used in limestone-based wet-scrubbing systems (fig. 4). Ordovician limestone is mined in north-central Kentucky for the production of scrubber lime.

In Illinois, Ordovician and Silurian dolomites crop out in large areas in the northern part of the state. Large areas of Mississippian limestone and smaller areas of Ordovician, Silurian, and Devonian limestone are found along the Mis-

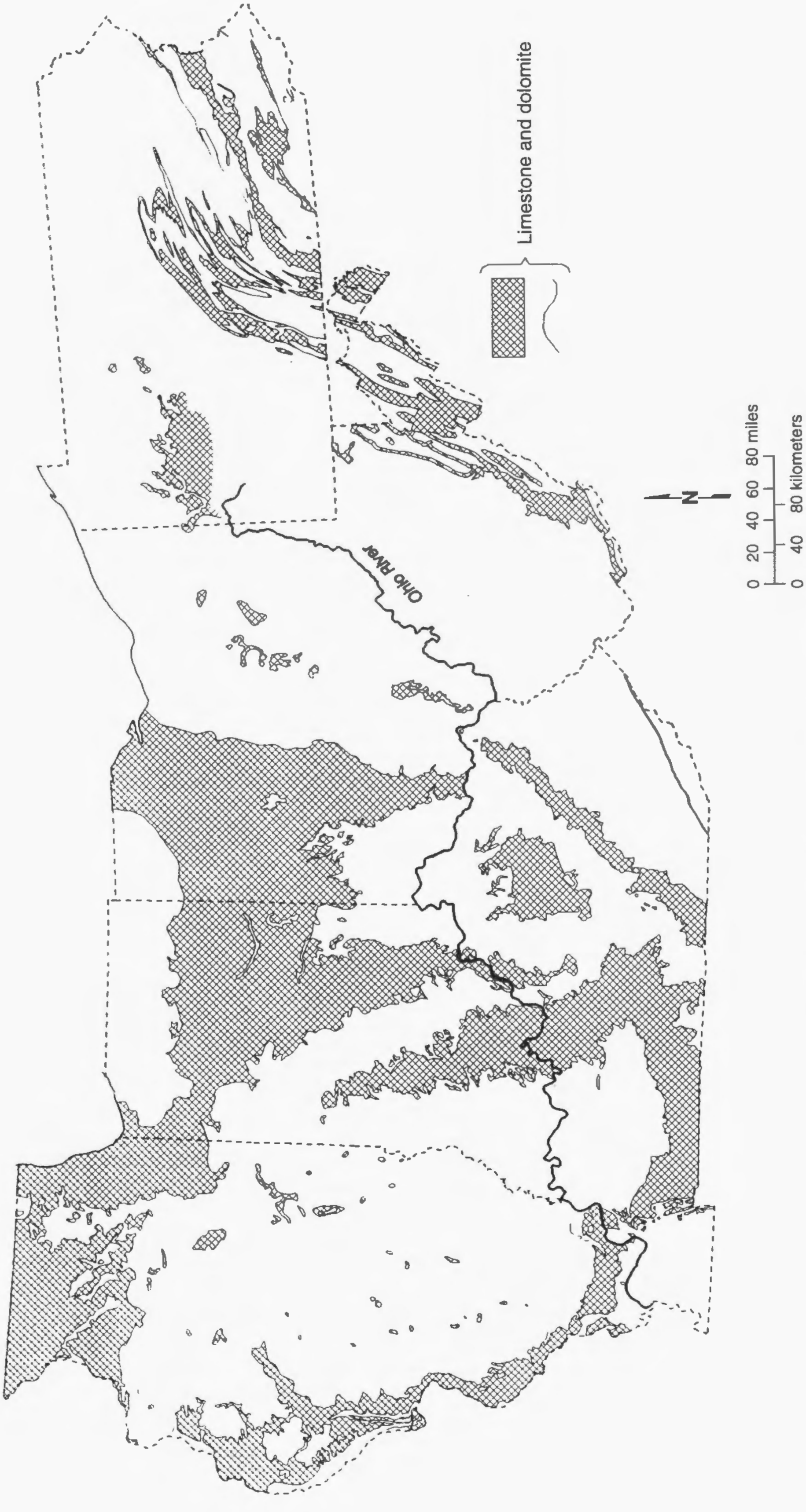

FIGURE 3.—Outcrop area of limestone and dolomite in the Ohio River Valley.

FIGURE 4.—Four limestone-based scrubbers at the Louisville Gas and Electric Company Mill Creek Station, Jefferson County, Kentucky. Scrubbers use Ste. Genevieve Limestone (Mississippian) from western Kentucky.

sissippi and Ohio Rivers in western and southern Illinois. Small areas of relatively thin Pennsylvanian limestone occur in central Illinois.

NEED FOR GEOLOGIC MAPPING OF CARBONATE ROCKS

A geologic map can be thought of as a visualization of the three-dimensional distribution of bedrock and surficial formations containing the mineral resources used every day. A basic bedrock-geologic map shows the areal extent of the various rock formations that crop out along Earth's irregular surface. Surficial-material maps show the distribution of unconsolidated deposits such as glacial till, alluvium, and colluvium. These basic geologic maps are the fundamental and essential starting point for all land-use and mineral-resource choices that need to be made now and in the future. These issues include environmental protection, hazard remediation, energy production, and infrastructure maintenance, to list a few.

The status of existing bedrock-geologic maps for the six states of the Ohio Valley Mineral Consortium is outlined in table 1. All of the states have small-scale statewide bedrock maps of varying vintages and compilation detail. The status of geologic mapping in the six Ohio Valley states is fairly typical of the nation with the exception of Kentucky. It is the only sizeable state in the nation that is completely mapped at the scale of 1:24,000. Detailed geologic mapping of most states ranges widely in the detail at which it was done and the time of the mapping effort. All of the state geological surveys in the Ohio Valley agree that detailed geologic mapping at the scale of 1:24,000 is necessary to provide the kinds of geologic data, including the accurate location of limestone resources, needed for today's land-use and mineral-resource decisions.

Detailed geologic mapping in limestone and dolomite terrains provides a wealth of information critical to the successful location and development of new carbonate-rock resources. Detailed mapping also provides important new data that are exceedingly beneficial in expanding existing quarry operations. By knowing the three-dimensional geologic framework of a specific site or a large region, the limestone or dolomite producer is armed with a predictive capability that will save thousands or millions of dollars when developing new operations.

Vertical and lateral stratigraphic relationships among formations and members are determined by detailed geologic mapping. Identification of breaks (unconformities) in vertical sedimentary-rock successions allows accurate prediction of missing units at some distance from existing operations. Determination of lateral changes in aspect of limestone or dolomite formations permits accurate prediction of changes in rock quality and can save tremendous amounts of money and time during exploration for high-quality materials. Changes in thickness of quarry layers can be predicted through the development of isopach maps.

Detailed geologic mapping also provides an accurate picture of structural fabrics such as fractures, faults, folds, and secondary mineralization that affect the spatial distribution and engineering characteristics of quarry layers. A solid understanding of the structural geology of an area is critically important to the development of an efficient mining

TABLE 1.—*Status of bedrock geologic mapping in the Ohio Valley states*

State	% mapped	Scale	Vintage/comments
PA	50	mixed—1:24K, 1:50K, 1:62.5K	1920's to present
	remainder	1:24K & 1:62.5K	Preliminary compilations (Map 61) for 1980 statewide map
WV	10	1:24K	1980's & 1990's—published and open-file maps
	remainder	1:62.5K	County reports—1900 to 1930
OH	5	various—generally 1:62.5K	1918 to 1977—county bulletins (and USGS Professional Papers)
	2	various—1:62.5K to 1:200K	1940's & 1950's—county water bulletins
	3	1:24K to 1:62.5K	1980's detailed mapping—open-file & manuscript maps
	75	1:24K	1990's open-file (COGEOMAP/STATEMAP) reconnaissance maps for new statewide bedrock map
	remainder	1:62.5K	1900 to 1920—unpublished compilation quadrangles for 1920 state map
IN	10	1:24K	Current efforts—COGEOMAP
	remainder	1:24K	Field and compilation sheets for statewide maps (to group level only)
KY	100	1:24K	1960 to 1978 (only state completed at this scale)
IL	<20	various—generally 1:62.5K	County Resource—Geology for Planning maps
	4	1:24K	1940 to present
	remainder	1:62.5K	Compilation sheets for 1967 state map

plan. An understanding of the three-dimensional arrangement and intersection of bedding surfaces and fractures is quite important in being able to predict rock fragmentation characteristics and movement of ground water in a quarry operation.

Another product resulting from detailed geologic mapping is the development of depth-to-bedrock maps. Such maps are pivotal in determining whether or not it is cost effective to open a new quarry and remove a thickness of surficial material to get at the limestone or dolomite.

In addition to mineral-resource development issues, growing environmental-quality concerns have caused a pressing need for geologic mapping in carbonate-rock terrains and other settings. Waste management, both surface and subsurface, requires detailed geologic data to prevent future remediation efforts that are even costlier than the original disposal costs. Landfills require information on the surficial and bedrock geology to effectively contain waste and prevent ground-water contamination. Waste-disposal wells for both hazardous and nonhazardous liquids require geologic-map information identifying the porosity and permeability of potential subsurface injection zones to insure that the wells will meet permitting standards. Additional information is needed on the depth and extent of underground sources of drinking water and on the character and availability of low-permeability confining zones to isolate injected wastes. Construction and infrastructure development require data on the surficial and shallow subsurface materials to plan for foundations, drainage, and sewer construction. Additional water resources are continually needed for the growing population of the Ohio Valley. Geologic mapping is an essential element in locating new and expanded sources of ground water.

Geologic-hazard planning and remediation is another field with a great need for modern, detailed geologic maps. Landslides cost millions of dollars annually to repair or replace affected buildings, roadways, and other structures. Up-to-date mapping of slide-prone materials identifies existing risk areas and greatly helps planning for future construction to eliminate or avoid problems. Indoor radon derives from underlying surficial materials and/or bedrock. Detailed geologic maps enable planners, developers, and builders to cope with indoor radon. Liquefaction is a potential concern for certain low-strength materials such as silt and sand deposits or sinkhole-fill materials. These materials can rapidly lose bearing capacity in the event of a major earthquake. Detailed mapping of surficial materials is a crucial need as more is discovered about the seismic history and potential for earthquakes in the central U.S.

Energy production is currently in worldwide turmoil. Some researchers regard use of hydrocarbon fuels as potentially contributing to an increase in the Earth's atmospheric temperature and to acid rain. Nuclear power has not overcome a myriad of mechanical and environmental problems, along with severe public skepticism. However, at the current time, there are no known economically viable alternative energy sources to replace all the coal, oil, and natural gas being used. Detailed bedrock mapping identifies additional sources of coal, particularly the low-sulfur seams that are currently needed. Subsurface geologic mapping is critical for identification of additional domestic reserves of oil and gas. Most significantly, the mapping and characterization of carbonate resources in the Ohio Valley will have a big impact on enlarging their utility as chemical reagents in the production of energy.

Finally, dealing with our aging infrastructure will require large quantities of industrial minerals. Many of the nation's roads, bridges, sewer systems, and buildings currently require repair or replacement. Most of the needed construction aggregates are high-volume, low-value commodities. As urban areas expand and encroach upon metropolitan sources of aggregate, the cost of these materials goes up greatly owing to increased transportation from more distant sources. Detailed geologic mapping of carbonate rocks is essential for efficient zoning and planning for the conservation and orderly use of aggregate resources.

Enactment of the National Cooperative Geologic Mapping Program of 1992 (Public Law 102-285) was an indication of the widespread national need and support for detailed geologic mapping. Mapping of carbonate rocks in particular is needed in the Ohio River Valley region in order to identify the location of these resources and assure their availability for future generations.

LIMESTONE AND DOLOMITE QUALITY DISTRIBUTION

Maps in figures 5, 8, 11, and 12 show the principal outcrop areas of formations containing high-purity dolomite, high-calcium limestone, and other levels of calcium carbonate content in limestones of the Ohio Valley. In most cases, areas depicted are the outcrop of rock formations that contain mineable thicknesses of the indicated quality level. It should not be implied that the particular purity of carbonate rock underlies every square mile of the mapped areas.

Many carbonate rock units have a varied composition, both laterally and vertically. The quality of stone produced at most sites depends upon the thickness of quarry layers mined. Selective quarrying can raise or lower the level of calcium carbonate produced by including or eliminating beds that have more or less dolomite or that have significant insoluble residues. Limestone and dolomite availability also are affected by two other conditions: subsurface occurrence and overburden thickness. From a positive viewpoint, many of the formations that crop out in this region have good potential for providing high-quality stone from shallow underground mines. Such mines would range from drift mines adjacent to deep surface quarries or located in deep valleys to shallow slope mines several tens of miles downdip from an outcrop belt. In a restrictive note, much of the dolomite in northern and western Ohio, northern Indiana, and northeastern Illinois is covered by varied thicknesses of unconsolidated glacial sediments. Availability of stone in these regions is largely governed by the depth to bedrock.

Figure 5 shows the general location of high-purity dolomite formations in the Ohio Valley. These rocks contain, or consist wholly of, nearly stoichiometric dolomite with less than 5 percent insoluble materials. Making up the largest single area by quality, these rocks are primarily flat-lying Silurian dolomites in Ohio (fig. 6) and Indiana and Silurian and Ordovician dolomites in Illinois. Many of the Silurian rocks are mixtures of reef, reef-flank, and interreef deposits that range from 100 to more than 500 feet thick. The Cambrian dolomite units in southeastern Pennsylvania and the far eastern panhandle of West Virginia (fig. 7) can be as much as 1,000 feet thick but are areally restricted by the complex structural conditions in the Piedmont (multiple events of deformation) and Valley and Ridge Physiographic Provinces.

Figure 8 represents the outcrop of formations that contain mineable thicknesses of limestone with >95 percent $CaCO_3$. Several Cambrian to Devonian formations in narrow bands in structurally complex southeastern and central Pennsylvania and eastern, southeastern, and far southern West Virginia contain zones of high-calcium marble (in Pennsylvania) and limestone from 30 to 200 feet thick. Thin high-calcium zones up to 25 feet thick occur in the Silurian and Devonian rocks in southwestern and northwestern Ohio. Several Mississippian formations in Kentucky and southern Indiana (fig. 9) contain zones of calcarenitic and oolitic high-calcium limestone. These zones occur discontinuously throughout the outcrop area shown and commonly range from 10 to 100 feet thick. An additional area of stone occurs in north-central Indiana. This area marks the known extent of undolomitized reefs in the Silurian rocks of Indiana. Some isolated high-calcium limestone reefs more than a mile in diameter occur in this region of high-purity Silurian dolomite. Many Mississippian as well as some Ordovician to Devonian formations in western and southern Illinois contain zones of high-calcium limestone from 25 to more than 100 feet thick. For example, the high-calcium Mississippian-age Ullin Limestone (fig. 10) is quarried in southern Illinois for scrubber stone and other uses.

Lowering $CaCO_3$ quality from 95 percent to 90 percent greatly increases resources but that fact is not readily apparent in much of figure 11. The large increase in carbonate-rock outcrop in central and southeastern Pennsylvania generally has some potential for 90 to 95 percent $CaCO_3$. The additional area in western Pennsylvania represents the Vanport Limestone. This unit is generally >90 percent $CaCO_3$, low in magnesium, and 5 to 20 feet thick. The overall outcrop area in West Virginia locally has mineable thicknesses of >90 percent $CaCO_3$ stone, and rarely has mineable thicknesses of >95 percent $CaCO_3$. Scattered areas of Silurian, Devonian, and thin Pennsylvanian limestones occur in Ohio. As noted at the start of this section, the quality of rock producible at most sites depends upon the thickness mined. The areas of high-calcium stone shown unchanged from figure 8 to figure 11 in Indiana, Kentucky, and Illinois would contain much greater resources of >90 percent $CaCO_3$ stone by consideration of increased thicknesses at the lower quality.

Further lowering the $CaCO_3$ quality to 85 percent increases the potential areas to almost the entire limestone outcrop areas of the Ohio Valley (fig. 12). Three small areas are added in southeastern Pennsylvania in addition to the

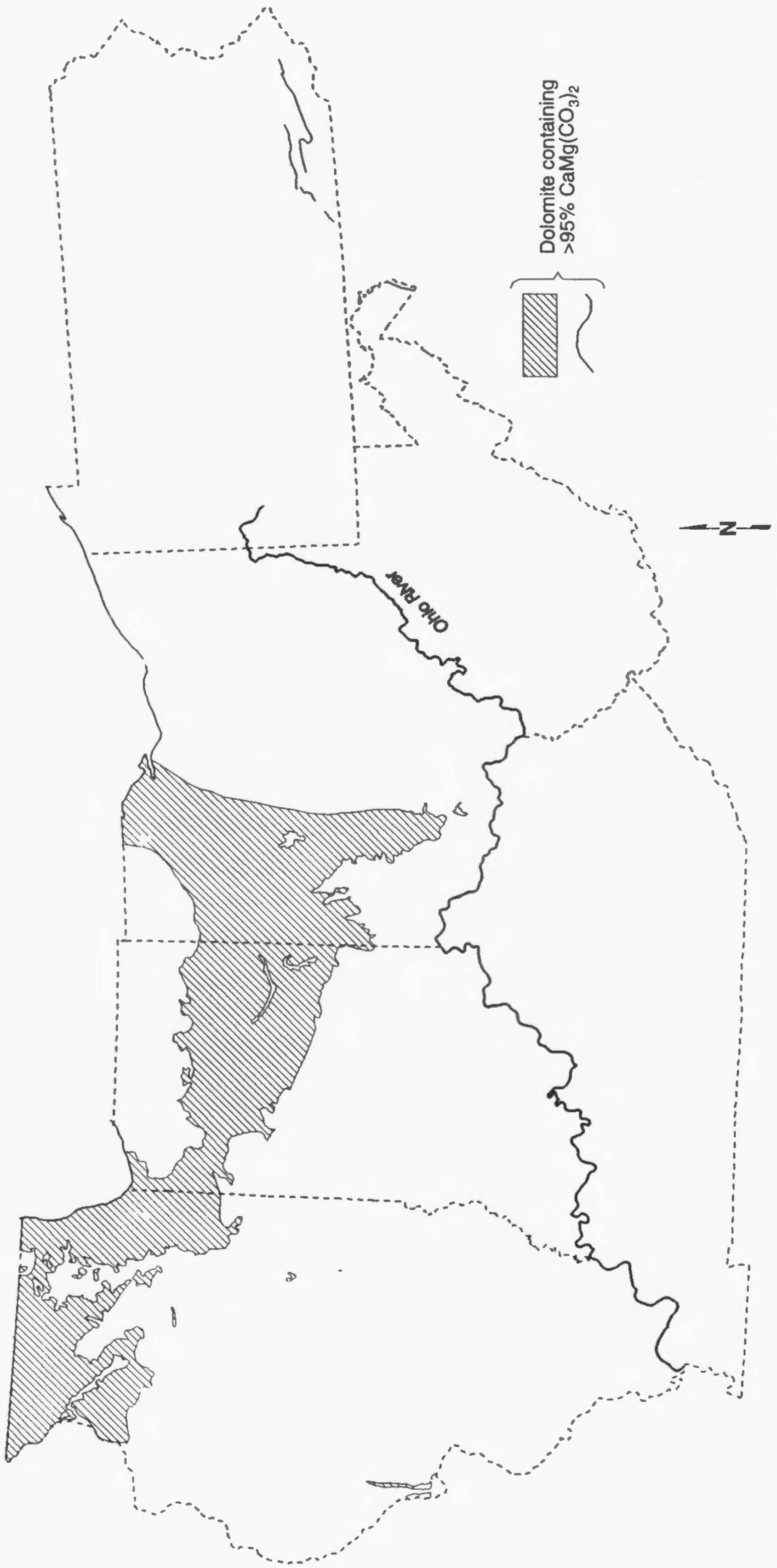

FIGURE 5.—Outcrop area of high-purity dolomite in the Ohio River Valley.

FIGURE 6.—Quarry of the Plum Run Stone Division of Davon, Inc., in Adams County, Ohio. The quarry produces high-purity dolomite from the Peebles, Greenfield, and Tymochtee Dolomites (Silurian).

FIGURE 7.—The Millville Quarry near the town of Millville, Jefferson County, in West Virginia's extreme eastern panhandle. The Tomstown Dolomite (Cambrian) is quarried for aggregate and railroad ballast.

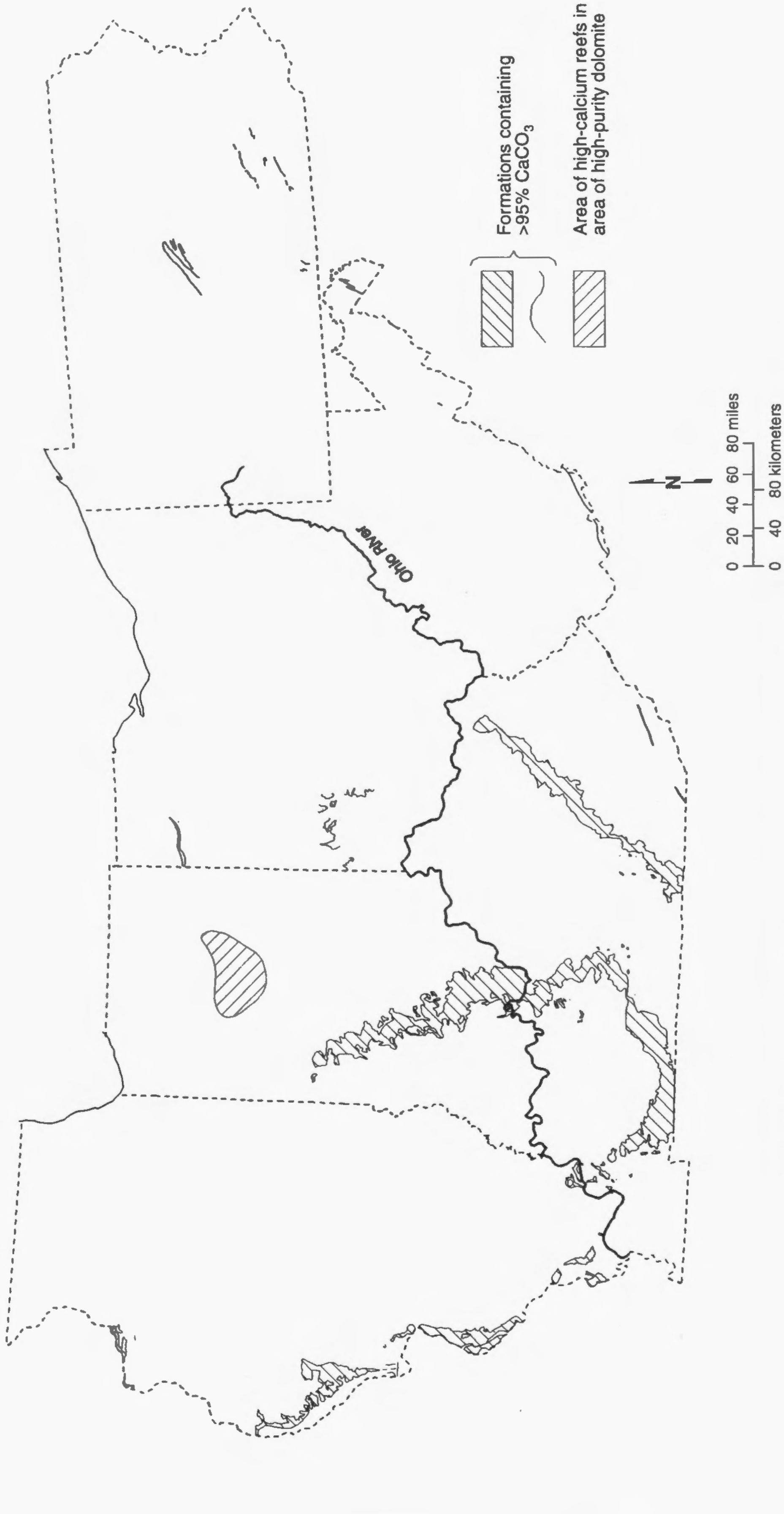

FIGURE 8.—Outcrop area of formations containing mineable thicknesses of limestone with >95 percent $CaCO_3$.

FIGURE 9.—The Cape Sandy Quarry of Mulzer Crushed Stone, Inc., on the Ohio River in Crawford County, Indiana. The quarry produces high-calcium limestone from the Paoli and Ste. Genevieve Limestones (Mississippian) and has direct barge loading on the Ohio River. Photograph courtesy of Mulzer Crushed Stone, Inc.

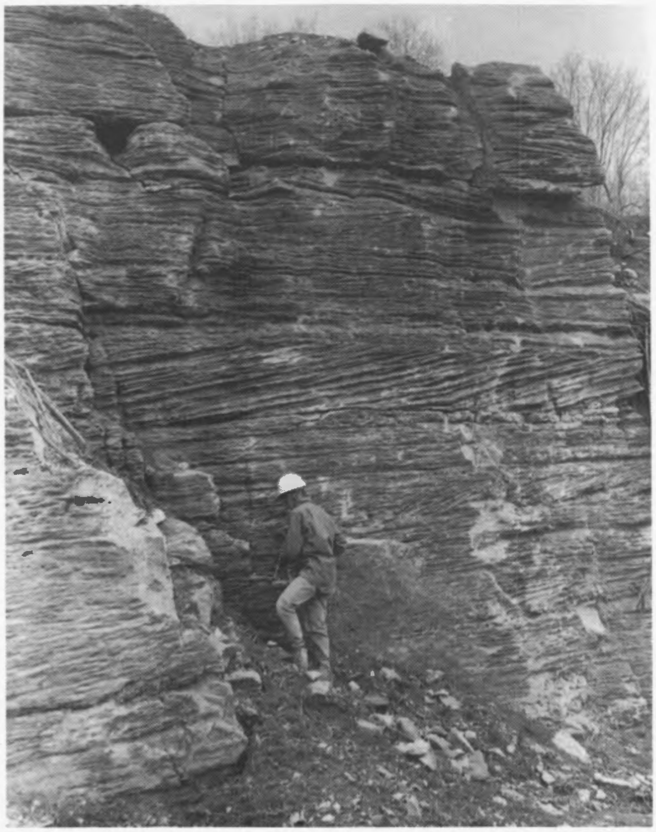

FIGURE 10.—A solution-etched, nearly vertical fracture surface in the Ullin Limestone (Mississippian) in the upper bench of the Columbia Quarry Company Jonesboro Quarry, 5 miles south of Jonesboro in Union County, Illinois. Solution etching of the joint surface has highlighted the relatively thick bedded and cross-bedded character of the limestone. Because of these and other features, including widely spaced joints and an attractive color, the Ullin Limestone has been quarried for building stone nearby.

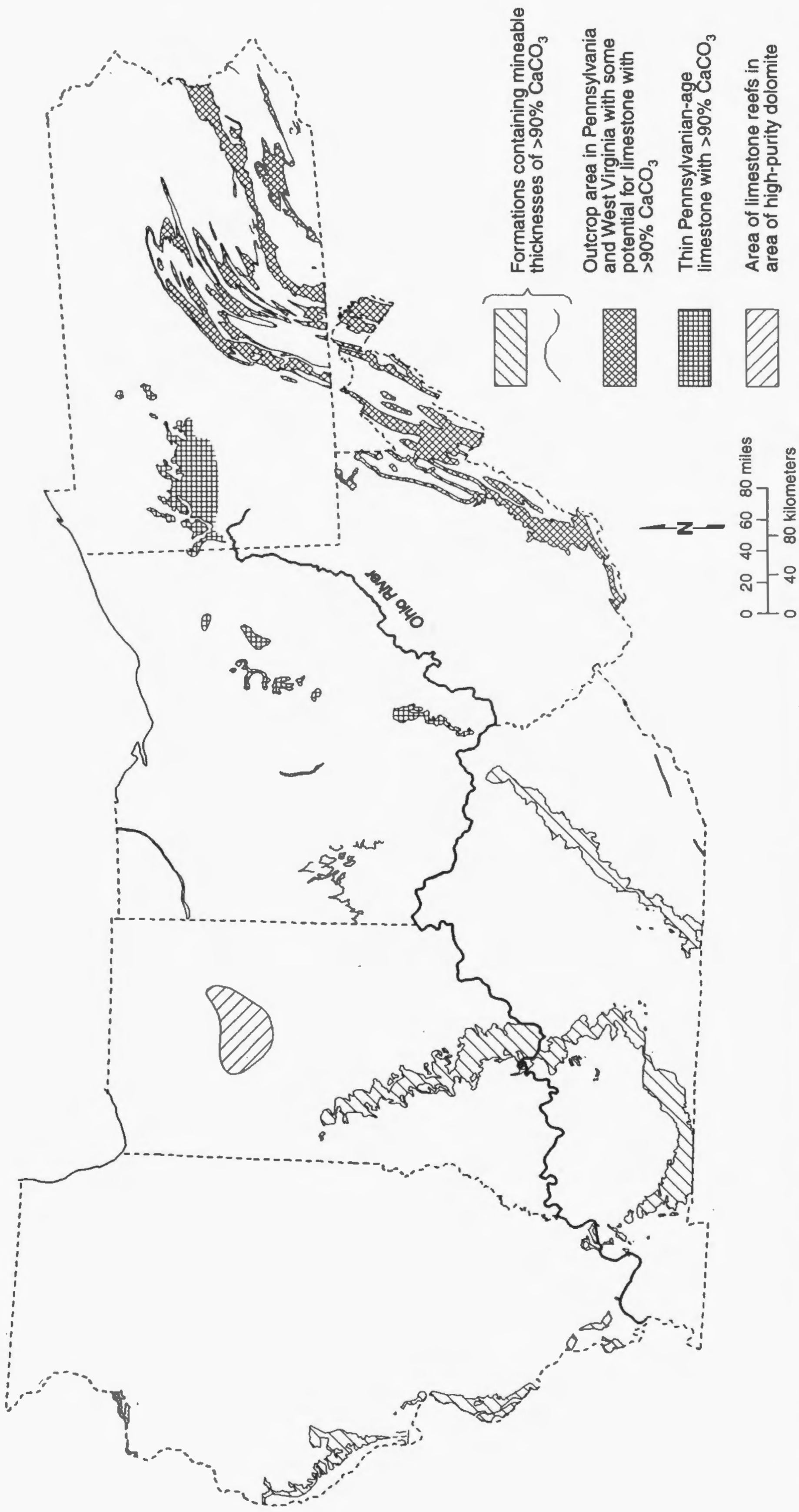

FIGURE 11.—Outcrop area of formations containing mineable thicknesses of limestone with >90 percent $CaCO_3$. Scattered units in West Virginia have >90 percent $CaCO_3$; a few units have >95 percent $CaCO_3$.

potential resource increase in those areas already shown as >90 percent. The outcrop area in West Virginia commonly has mineable thicknesses >85 percent $CaCO_3$. There is a small increase in the available area of Devonian limestone in central Ohio and Silurian limestone in southwestern Ohio. North-central Kentucky has an area of Ordovician limestone and both Indiana and Kentucky have a widespread increase in the outcrop available from Mississippian limestones. The large addition in central to southeastern Indiana is a region of Silurian and Devonian rocks that contains interbedded high-calcium limestone, high-purity dolomite, calcitic dolomite, and other silty and cherty carbonates that vary both vertically and laterally. Finally, Illinois shows a large increase in available outcrop. This area includes several formations of Ordovician to Pennsylvanian, but mainly Mississippian, age. In places some units may be moderately to highly dolomitic. In many places multiple Mississippian limestones are thicker than 25 feet but may be separated by sandy, silty, cherty, or shaly units.

QUALITY AND QUANTITY DATA AVAILABLE AT STATE GEOLOGICAL SURVEYS

The state geological surveys are the repository for all types of data on the mineral resources of their state. These data exist in many forms. The states of the Ohio Valley Mineral Consortium publish the results of research investigations in various formats ranging from single-page fact sheets to thick and comprehensive bulletins (see "Selected references" for examples). In addition to published information, most states have massive volumes of data available on open file for inspection at the survey office or for copying and dissemination. These data can be in the form of maps, reports, core descriptions, measured sections, physical test reports, chemical analyses, or computer databases. Thousands of feet of well cuttings and core also are available for inspection.

Specific chemical information on limestone and dolomite available in the Ohio River Valley is shown in table 2. The number of individual chemical analyses varies from state to state and ranges from 1,000 to over 6,000. The age of the rock represented by analyses also varies and, to a large extent, mirrors the age of the carbonate rocks that crop out at the surface in each state.

Reserve tonnages like those calculated for individual coal seams generally are not determined for carbonate rocks. However, much of the data available can be used to estimate reserves. Research reports on carbonate formations generally list thickness data or contain isopach maps. Most of the chemical data described above represents specific thicknesses. In addition, many of the thousands of measured sections on file at the surveys list thicknesses of carbonate units. Table 3 shows the areas required to produce 100,000 tons of rock per year at several specific thicknesses of limestone and dolomite. Anyone desiring information on the location, quality, and quantity of carbonate rock available in any specific region should contact the appropriate state geological survey at the following locations:

Illinois State Geological Survey
Illinois Department of Natural Resources
Natural Resources Bldg.
615 East Peabody Drive
Champaign, IL 61820-6964
Phone (217) 244-6944 FAX (217) 333-2830

Indiana Geological Survey
Indiana University
611 North Walnut Grove
Bloomington, IN 47405-2208
Phone (812) 855-2687 FAX (812) 855-2862

Kentucky Geological Survey
University of Kentucky
228 Mining and Mineral Resources Bldg.
Lexington, KY 40506-0107
Phone (606) 257-5500 FAX (606) 257-1147

Division of Geological Survey
Ohio Department of Natural Resources
4383 Fountain Square Drive, B-2
Columbus, OH 43224-1362
Phone (614) 265-6602 FAX (614) 447-1918

Bureau of Topographic and Geologic Survey
Pennsylvania Department of Conservation and Natural Resources
P.O. Box 8453
Harrisburg, PA 17105-8453
Phone (717) 787-5828 FAX (717) 783-7267

West Virginia Geological and Economic Survey
P.O. Box 879
Morgantown, WV 26507-0879
Phone (304) 594-2331 FAX (304) 594-2575

TABLE 2.—*Carbonate chemical analyses available at Ohio Valley geological surveys*

Geologic system	No. of analyses, by state					
	IL	IN	KY	OH	PA	WV
Pennsylvanian	130	40	0	150	100	240
Mississippian	540	2,200	3,990	20	30	1,140
Devonian	30	850	0	210	5	280
Silurian	200	2,400	180	1,550	75	260
Ordovician	100	450	2,000	180	600	560
Cambrian	0	20	0	0	300	80

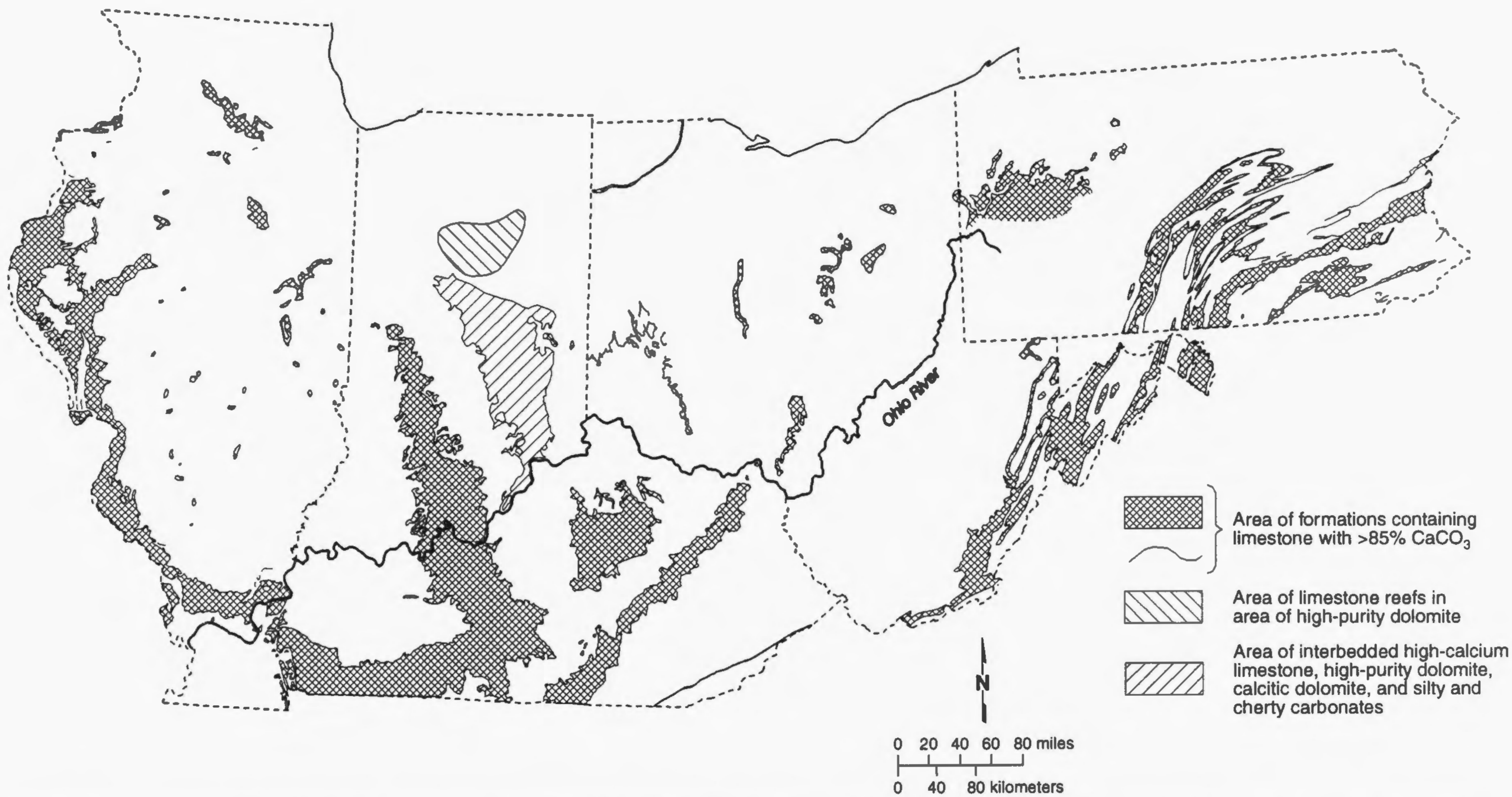

FIGURE 12.—Outcrop area of formations containing mineable thicknesses of limestone with >85 percent $CaCO_3$. Illinois units include those >25 feet thick, but separated by sandy, silty, cherty, or shaly units. Some Illinois units may be highly dolomitic.

TABLE 3.—*Area needed to provide 100,000 tons of carbonate rock per year versus thickness of deposit*

Limestone		Dolomite	
Thickness of deposit (feet)	Acres needed	Thickness of deposit (feet)	Acres needed
5	5.6	10	2.6
10	2.8	25	1.03
20	1.4	50	0.51
50	0.56	100	0.26
100	0.28	150	0.17

CHEMICAL ANALYSIS METHODS AND RECOMMENDATIONS

ASTM COMMITTEES

The American Society for Testing and Materials (ASTM) is a nationwide scientific organization that issues voluntary consensus standards on a wide range of products, materials, and services. These standards can take the form of test methods, practices, classifications, specifications, terminology, and guides. The standards are contained in more than 65 volumes which are revised annually.

The ASTM functions through more than 130 committees and over 2,000 subcommittees. Most of the ASTM standards applicable to limestone use as a chemical are the responsibility of ASTM Committee C-7 on Lime and specifically Subcommittees C07.03 on Industrial Uses, C07.05 on Methods of Test, C07.06 on Physical Tests, and C07.09 on Research. Chairpersons for these four subcommittees were contacted for this report to obtain their views of the latest information on testing methods for carbonate rocks. The rest of this section is a brief review of this telephone survey (Scott Berman, Gwen Palmer, Dewey Stanley, and Dan Walker, personal commun., 1993).

ASTM Standard C25, Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime (ASTM, 1995), contains numerous methods for chemical analysis of limestone. Most of these elemental methods are classical wet chemical methods, either gravimetric or volumetric. There is an alternative wet chemical method using titration that is much simpler than gravimetric methods and is generally quite precise, especially for calcium. Another standard (at the subcommittee ballot stage in 1995) is being developed on test methods for dissolved calcium and magnesium.

There is currently a Task Group in Subcommittee C07.05 working on X-ray methods. This work has been released as ASTM Standard C1271, Standard Test Method for X-ray Spectrometric Analysis of Lime and Limestone (ASTM, 1995). The Task Group will address techniques for specific elements in the near future. Another new Task Group has recently developed a standard test method for inductively coupled plasma (ICP) spectrometry. This method has been accepted and will be released in 1996 as ASTM Standard C1301 (Dewey Stanley, personal commun., 1995). Both Standards C1271 and C1301 will consist of standard preparation techniques and wavelength tables initially. Round-robin testing of standard samples is planned for 1996 to develop precision and bias statements for both of these methods.

A new section on performance requirements is being developed for ASTM Standard C25. This will be similar to a section in ASTM Standard C114, Standard Test Methods for Chemical Analysis of Hydraulic Cement (ASTM, 1995). These sections list the replicate testing and permissible variation requirements to approve any test method (including instrumental ones) to be used for elemental analysis as long as the results can be tracked back to certified standard samples.

In 1992, the ASTM adopted a test on Limestone Grindability. This test is now included in ASTM Standard C110, Standard Test Methods for Physical Testing of Quicklime, Hydrated Lime, and Limestone (ASTM, 1995). The recommended method uses a standard laboratory-scale ball mill to measure stone grindability. The responsible ASTM subcommittee had evaluated tests for Bond Work Index and decided the method was too cumbersome for small labs and effective quality control. The method that was adopted had been originally proposed by the Electric Power Research Institute (EPRI) and Radian Corporation as an effective substitute for limestone grindability.

The ASTM subcommittees for lime and limestone have not yet looked at reactivity testing of limestone and are not aware of anyone in the ASTM structure that is evaluating reactivity for SO_2 control. The subjects of grindability and reactivity are likely candidates for future research.

ANALYTICAL METHODS

As indicated above, most of the ASTM-recommended methods for limestone chemical analysis are gravimetric in nature. Although these methods can be very accurate and precise, they are intended for referee or certification use and can be too cumbersome and technical for routine work. Probably the best single method combining speed and accuracy would be the alternative titration method for calcium and magnesium listed in ASTM Standard C25. This is a rapid complexometric method using ethylenediaminetetraacetic acid (EDTA). Repeatability and reproducibility of the method are very close to traditional gravimetric methods. Because this method is not an instrumental one, it can be used in small labs with little initial investment.

X-ray fluorescence and ICP are both instrumental techniques that can be run in an automated configuration, which allows many samples to be processed in a short period of time. X-ray methods generally do not directly measure absolute elemental quantities. Known standard materials of varying elemental concentrations commonly are used with complex equations (algorithms) to calculate the individual sample analyses. With the proper technique and standard material selection, accurate analyses can be performed either in an individual or multi-element mode. ICP also uses standard calibration materials but is a solution-based spectrometer method. The ICP can be remarkably accurate, particularly for minor and trace element analyses. Care must be taken with the procedure to insure accuracy for major elements such as calcium in limestone and calcium and magnesium in dolomite.

Atomic absorption spectrometry (AAS) is the fourth method commonly used for chemical analysis of carbonate rocks. Although this instrumental procedure has been around for a long time it is not necessarily the best choice for calcium determinations. AAS can be very accurate for elements in lower concentrations, but it is more sensitive to chemical and ionization interferences than ICP. The extra dilutions required to determine major elements such as calcium can cause problems with the method. Additionally, the steps required to increase the accuracy of the method can involve running a sample twice to get a final analysis.

STEPS TO ASSURE ANALYTICAL QUALITY

There are a number of methods available for the chemical analysis of limestone and dolomite. Many of them have specific published procedures issued by one agency or another such as the ASTM. Most of the methods have particular strong points as well as drawbacks. However, the simplest way to obtain an accurate chemical analysis of a carbonate rock may involve a company's laboratory selection and sample submission procedures rather than their selection and specification of a certain analytical method. The following steps can be used, at least in some detail, to insure that meaningful numbers are obtained, whether from a contract lab or by in-house analyses.

The first suggestion would be applicable to companies wanting to purchase analytical services rather than to set up their own lab. Find out if the proposed lab is familiar with whole-rock chemical analysis in general and carbonate-rock analysis in particular. A lab that specializes in water samples or environmental samples, for example, may be a very competent laboratory. If, however, they are not familiar with whole-rock analyses, they may not be aware of all the potential problems. Also, check whether or not the laboratory participates in any round-robin testing and evaluation procedures, a practice that is very desirable. Do they compare their results on split samples analyzed by other labs using similar or different analytical techniques?

Next, the utilization of quality-assurance (QA) and quality-control (QC) procedures will increase the accuracy and reliability of chemical analysis determinations. For purchased services find out what QA/QC practices the proposed lab follows. Ask if they can provide you with examples of their control charts showing the day-to-day analytical variations.

The rest of the suggested steps would be applicable both to contract services or to in-house analyses. Commercial standard reference materials (SRM) are available from a number of different agencies such as the National Institute of Standards and Technology (NIST; formerly the National Bureau of Standards). These materials, which include limestone and dolomite, are sold with a certificate of elemental composition. The issuing agencies have used great care in the preparation, packaging, and analysis of these materials. Selected samples of these materials should be analyzed with each batch of samples run by any procedure. Careful monitoring of the SRM results will show any deviations from the certified values.

In addition to the use of SRM's, sample duplication should be used. A laboratory should commonly run a certain number of submitted samples in duplicate to assure the values fall within accepted replication limits. Similarly, a company should submit a certain number of blind duplicates for analysis—that is, split portions of a single sample should be submitted with different sample numbers, known only to the submitter, not to the laboratory.

The use of matrix matching in the preparation of calibration standards should be followed for many of the instrumental analytical methods. Matrix matching consists of the selection of standard materials or the preparation of solutions so that the calibration standards have a composition similar to the samples to be analyzed. For example, use magnesium in the solutions for dolomite samples; use silicon and aluminum in the solutions for analysis of argillaceous carbonate rocks; don't use dolomites and shales as standards for analysis of high-calcium limestone samples.

Another consideration is to do whole-rock analyses on some samples. Limestone and dolomite are made up of more than $CaCO_3$ and $MgCO_3$. In addition to the QA/QC practices described above, the determination of most of the common elements in a carbonate rock give another tool to evaluate analysis quality. A determination of calcium, magnesium, silicon, aluminum, iron, sodium, potassium, sulfur, and possibly manganese and strontium will permit a mineralogical calculation of whole-rock composition that should account for essentially 100 percent of a sedimentary carbonate rock. If this calculation falls outside the range of 98 to 102 percent, there is a great likelihood that one or more of the elements are in error. The completion of a whole-rock analysis on selected samples in conjunction with analysis of SRM's and duplicate analyses would provide considerable analytical reliability to those companies that feel they only need calcium determinations on most samples.

All parties to a contract to supply limestone or dolomite for sulfur-sorbent use should realize that there is some variability inherent in any analytical method. Utilities should determine the minimum chemical quality they require and set their specifications accordingly. Laboratories and stone suppliers should list the standard deviation of their analytical data. The role and effect of variation should be discussed ahead of time so that both groups are talking the same language. Suppliers should analyze a sufficient number of samples so that they can accurately characterize their day-to-day product. It is no longer sufficient to rely on 10- or 20-year-old analyses to represent a product. Limestone and dolomite as rocks are simply too heterogeneous for that.

A final point about carbonate chemical characterization is representative sampling. Representative sample collection and proper preparation are the foundation to meaningful analyses. Whether samples are obtained from drill core, stock piles, ledge rock, or production belts, it is imperative that representative statistical sampling techniques are used to cut down on possible variance. Once the sample is collected, proper reduction techniques such as riffle splitting must be used. In short, every effort must be made to make sure the final sample submitted for analysis is actually representative of a highwall, a production run, or a shipment of stone.

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